

10/049606
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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

ATTORNEY DOCKET NUMBER IN-5555	U.S. APPLICATION NO (IF KNOWN SEE 37 RR 15) 10/049606	
INTERNATIONAL APPLICATION NO PCT/EP00/07990	INTERNATIONAL FILING DATE 16. August 2000 (16.08.2000)	PRIORITY DATE CLAIMED 16. August 1999 (16.08.1999)
TITLE OF INVENTION: COATING MATERIAL AND ITS USE FOR PRODUCING HIGHLY SCRATCH RESISTANT MULTILAYER TRANSPARENT LACQUERS		
APPLICATION(S) FOR DO/EO/US: Ulrike RÖCKRATH, Hubert BAUMGART, Andrea ZUMBRINK, Stefan SILBER and Thomas FARWICK		

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:


1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371 (b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ are transmitted herewith (required only if not transmittal by the International Bureau).
 - b. ☒ have been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(C)(2)).
7. ☒ Amendment to the claims of the International Application under PCT Article 19 (35 U.S.C.371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annex to the International Preliminary Examination Report under PCT Article 36

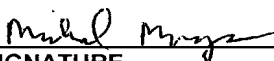
Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
13. ☒ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A Change of power of attorney and/or address letter.
16. ☒ Other items or information:

**A copy of the cover sheet from the PCT Published Application
A copy of the cover sheet from the Priority Document**

I hereby certify that the attached correspondence is being deposited with the United States Postal Service in an envelope as "Express Mail Post Office to Addressee" Mailing Label No. **EH799045260US** addressed to the Commissioner for Patents, Washington, DC 20231 on February 14, 2002.


Marjorie Ellis

U.S. APPLICATION NO. (If known see 37 CFR 1.50) 10/049606		INTERNATIONAL APPLICATION NO. PCT/EP00/07990		ATTORNEY'S DOCKET NUMBER IN-5555	
17: <input checked="" type="checkbox"/> The following fees are submitted				CALCULATIONS PTO USE ONLY	
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) Nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO.....				\$970.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO.....				\$890.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.44(a)(2)) paid to USPTO.....				\$690.00	
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4).....				\$670.00	
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)				\$ 96.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$890.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	
Claims	Number Filed	Number Extra	Rate		
Total Claims	20 - 20 =	0	X \$ 18.00	\$	
Independent claims	01 - 03 =	0	X \$ 84.00	\$	
Multiple dependent claims(s) (if applicable)			+ \$280.00	\$	
TOTAL OF ABOVE CALCULATION =				\$890.00	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL =				\$890.00	
Processing fee of \$130.00 for furnishing the English translation later the [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$890.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$ 40.00	
TOTAL FEES ENCLOSED =				\$930.00	
				Amount to be: refunded	\$
				Charged	\$930.00
a. <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed.					
b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. 23-3425 in the amount of \$930.00 to cover the above fees A triplicate copy of this sheet is enclosed.					
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23-3425 . A triplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:					
BASF CORPORATION Patent Department 26701 Telegraph Road Southfield, Michigan 48034-2442 (248) 948-2355 Customer No. 26922			 SIGNATURE Michael F. Morgan Name 42,906 REGISTRATION NUMBER		

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Ulrike RÖCKRATH
Hubert BAUMGART
Andrea ZUMBRINK
Stefan SILBER
Thomas FARWICK

Serial No.: This application is a National
Phase of Patent Application
PCT/EP00/07990 filed 16 August 2000.


Filed: Thursday, February 14, 2002

For: COATING MATERIAL AND ITS USE
FOR PRODUCING HIGHLY SCRATCH
RESISTANT MULTILAYER
TRANSPARENT LACQUERS

Group Art Unit: Not Assigned

Examiner: Not Assigned

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20231 on February 14, 2002.


Marjorie Ellis

PRELIMINARY AMENDMENT UNDER 37 CFR § 1.115

Commissioner for Patents

Washington, D.C. 20231

Dear Sir:

This preliminary amendment is submitted with the application for entry into the U.S.
National Phase under Chapter II. This application is based on PCT/EP00/07990 filed on 16
August 2000.

In connection with the filing of this National Phase application, please make the
following preliminary amendments.

IN THE SPECIFICATION

After the title, please insert --This application is a National Phase Application of
Patent Application **PCT/EP00/07990** filed on 16 August 2000--

IN THE CLAIMS:

Please cancel claims 1-18.

Please add new claims 19-38.

19. (New) A coating material curable thermally and, if desired, with actinic radiation, comprising
- A) at least one binder containing at least two functional groups, and
 - B) at least one crosslinking agent containing at least two functional groups, wherein the functional groups of the binder are able to undergo thermal crosslinking reactions with complementary functional groups in the crosslinking agent, and the functional groups of the crosslinking agent are able to undergo thermal crosslinking reactions with complementary functional groups in the binder,
- and optionally at least one of,
- C) at least one constituent that is crosslinkable with actinic radiation,
 - D) at least one photoinitiator,
 - E) at least one thermal crosslinking initiator,
 - F) at least one reactive diluent curable by at least one of with actinic radiation and thermally,
 - G) at least one coatings additive, and
 - H) at least one organic solvent,
- wherein the at least one binder contains in copolymerized form at least one olefinically unsaturated polysiloxane macromonomer containing on average per molecule at least 3 double bonds.
20. (New) The coating material of claim 19, wherein the polysiloxane macromonomer contains on average per molecule at least 4 double bonds.
21. (New) The coating material of claim 19, wherein the polysiloxane macromonomer contains on average per molecule up to 10.5 double bonds.
22. (New) The coating material of claim 19, wherein the polysiloxane macromonomer contains on average per molecule from 5.5 to 6.5 double bonds.

23. (New) The coating material of claims 19, wherein the polysiloxane macromonomer has a number-average molecular weight M_n of from 500 to 100,000 daltons.
24. (New) The coating material of claim 19, wherein the polysiloxane macromonomer is in three-dimensionally crosslinked form.
25. (New) The coating material of claim 19, wherein the polysiloxane macromonomer is at least one of an alkylsiloxane resin, cycloalkylsiloxane resin, alkyl-arylsiloxane resin, alkyl-cycloalkyl-siloxane resin, cycloalkyl-aryl-siloxane resin, and arylsiloxane resin.
26. (New) The coating material of claim 25, wherein the alkyl radicals contain from 1 to 10 carbon atoms, the cycloalkyl radicals contain from 3 to 10 carbon atoms, and the aryl radicals contain from 6 to 12 carbon atoms.
27. (New) The coating material of claim 25, wherein the binder comprises an alkylsiloxane resin.
28. (New) The coating material of claim 19, wherein the polysiloxane macromonomer contains, as groups having olefinically unsaturated double bonds, at least one of acrylic groups, methacrylic groups, ethacrylic groups, vinyl groups, allyl groups, and crotonyl groups.
29. (New) The coating material of claim 19, wherein the polysiloxane macromonomer is present in at least one of the binders in copolymerized form in an amount up to 15% by weight of the binder.
30. (New) The coating material of claim 19, wherein the polysiloxane macromonomer is present in at least one of the binders in copolymerized form in an amount of at least 0.01% by weight of the binder.

31. (New) A multicoat clearcoat system for a primed or unprimed substrate, produced by a process comprising
- (1) applying at least one clearcoat film I of a coating material I curable thermally, and optionally with actinic radiation, to the surface of the substrate and at least partly curing it, and
 - (2) applying a further clearcoat film II of a coating material II curable thermally, and optionally with actinic radiation, to the surface of the at least one clearcoat film I, and
 - (3) curing by one of
 - (3.1) the at least one clearcoat film I and the clearcoat film II together if the at least one clearcoat film I was not previously fully cured, or
 - (3.2) the clearcoat film II alone if the at least one clearcoat film I was previously fully cured,wherein the curing is thermal and, optionally, with actinic radiation
- wherein at least one of the coating material I and the coating material II is a coating material of claim 19.
32. (New) The multicoat clearcoat system of claim 31, wherein the multicoat clearcoat system is one of an automotive OEM finish, an automotive refinish, an industrial coating, a coil coating a container coating, plastic coating, and a furniture coating.
33. (New) A process for producing a multicoat clearcoat system on a primed or unprimed substrate by
- (1) applying at least one clearcoat film I of a coating material I curable thermally, and optionally with actinic radiation, to the surface of the substrate and at least partly curing it, and
 - (2) applying a further clearcoat film II of a coating material II curable thermally, and optionally with actinic radiation, to the surface of the at least one clearcoat film I, and
 - (3) curing by one of
 - (3.1) the at least one clearcoat film I and the clearcoat film II together if the at least one clearcoat film I was not previously fully cured, or

(3.2) the clearcoat film II alone if the at least one clearcoat film I was previously fully cured,
wherein the curing is thermal and, optionally, with actinic radiation
wherein at least one of the coating material I and the coating material II is a coating material of claim 19.

34. (New) The substrate produced by the method of claim 33.
35. (New) A multicoat paint system for a primed or unprimed substrate, wherein the multicoat paint system is one of a color paint system, an effect paint system, and a color and effect paint system, produced by a process comprising
 - (1) applying at least one basecoat film III of a pigmented coating material III curable thermally, and optionally with actinic radiation, to the surface of the substrate, and drying it without curing, wherein the basecoat film is one of a color basecoat, an effect basecoat, and a color and effect basecoat,
 - (2) applying at least one clearcoat film I of a coating material I curable thermally, and optionally with actinic radiation, to the surface of the basecoat film III, and one of
 - (2.1) partly curing the at least one clearcoat film I alone,
 - (2.2) partly curing the at least one clearcoat film I together with the basecoat film III, or
 - (2.3) fully curing the at least one clearcoat film I together with the basecoat film III,wherein the curing is thermal and, optionally, with actinic radiation,
 - (3) applying a further clearcoat film II of a coating material II curable thermally, and optionally with actinic radiation, to the surface of the at least one clearcoat film I, and
 - (4) curing by one of
 - (4.1) the at least one clearcoat film I, the clearcoat film II, and the basecoat film III together if the at least one clearcoat film I and the basecoat film III were not previously fully cured, or
 - (4.2) the clearcoat film II alone if the at least one clearcoat film I and the basecoat film III were previously fully cured,

wherein the curing is thermal and, optionally, with actinic radiation,
wherein at least one of the coating material I and the coating material II is a coating material of claim 19.

36. (New) The multicoat paint system of claim 35, wherein the multicoat paint system is one of an automotive OEM finish, an automotive refinish, an industrial coating, a coil coating a container coating, plastic coating, and a furniture coating.
37. (New) A process for producing a multicoat paint system on a primed or unprimed substrate, wherein the multicoat paint system is one of a color paint system, an effect paint system, and a color and effect paint system, comprising
 - (1) applying at least one basecoat film III of a pigmented coating material III curable thermally, and optionally with actinic radiation, to the surface of the substrate, and drying it without curing, wherein the basecoat film is one of a color basecoat, an effect basecoat, and a color and effect basecoat,
 - (2) applying at least one clearcoat film I of a coating material I curable thermally, and optionally with actinic radiation, to the surface of the basecoat film III, and one of
 - (2.1) partly curing the at least one clearcoat film I alone,
 - (2.2) partly curing the at least one clearcoat film I together with the basecoat film III, or
 - (2.3) fully curing the at least one clearcoat film I together with the basecoat film III,wherein the curing is thermal and, optionally, with actinic radiation,
 - (3) applying a further clearcoat film II of a coating material II curable thermally, and optionally with actinic radiation, to the surface of the at least one clearcoat film I, and
 - (4) curing by one of
 - (4.1) the at least one clearcoat film I, the clearcoat film II, and the basecoat film III together if the at least one clearcoat film I and the basecoat film III were not previously fully cured, or
 - (4.2) the clearcoat film II alone if the at least one clearcoat film I and the basecoat film III were previously fully cured,

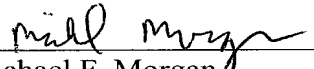
wherein the curing is thermal and, optionally, with actinic radiation,
wherein at least one of the coating material I and the coating material II is a coating
material of claim 19.

38. (New) The substrate produced by the method of claim 37.

REMARKS

Upon entry of the present amendment claims 19-38 are pending in the application. New claims 19-38 add no new matter, as these claims contain subject matter deleted from the canceled claims. There are one (1) independent claim and a total of twenty (20) claims pending in the application. Applicants respectfully request entry of the preliminary amendment.

Respectfully Submitted,


 Michael F. Morgan
 Registration No. 42,906

Date: February 14, 2002
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WO 01/12736

PCT/EP00/07990

**Coating material and its use for producing highly
scratch-resistant multicoat clearcoat systems**

The present invention relates to a novel coating
5 material curable thermally and, if desired, with
actinic radiation and also to a novel highly scratch-
resistant multicoat clearcoat system produced using it.
The present invention also relates to the use of the
novel highly scratch-resistant multicoat clearcoat
10 system in automotive OEM finishing and automotive
refinish, in industrial coating, including coil coating
and container coating, in the coating of plastics, and
in furniture coating. The present invention further
relates to a novel process for producing multicoat
15 clearcoat systems and multicoat color and/or effect
paint systems.

Automobile bodies, plastics parts for automobiles or
domestic appliances, and industrial components are
20 nowadays protected by a clearcoat. This clearcoat may
be used as the sole coating film or may form the
topmost coat of a multicoat color and/or effect paint
system. Automobile bodies in particular are very
extensively provided with a multicoat color and/or
25 effect paint system of this kind.

The requirements imposed on the resistance of coating
systems which are exposed to weathering, especially

insolation and acid rain, and also, even more frequently, to mechanical stress, especially that produced by wash-brush cleaning installations, are becoming increasingly stringent. This is so most particularly for vehicle finishes, which have to meet these requirements while also satisfying very high optical demands regarding gloss, surface smoothness, and color.

10 To date this problem has been solved by applying to the substrates a multicoat paint system which, in accordance with the heightened environmental compatibility requirements, is constructed in particular from aqueous coating materials. In the case of metal substrates, this system is produced, conventionally, from an aqueous electrocoat material, a water-based surfacer, a basecoat material, in particular an aqueous basecoat material, and a solventborne clearcoat material. The electrocoat material and the water-based surfacer are each baked following their application, and then form the primer system. The basecoat material, particularly the aqueous basecoat material, is applied to this system and dried. Over this film, which is not yet fully cured, the clearcoat material is applied, after which the two films are cured together (wet-on-wet technique). Where the substrates used comprise plastics, water-based primers are conventionally employed in place of the electrocoat materials.

The wet-on-wet technique for producing multicoat color and/or effect paint systems is described, for example, in the patents US-A-3,639,147, DE-A-3 333 072, 5 DE-A-38 14 853, GB-A-2 012 191, US-A-3,953,644, EP-A-0 260 447, DE-A-39 03 804, EP-A-0 320 552, DE-A-36 28 124, US-A-4,719,132, EP-A-0 297 576, EP-A-0 069 936, EP-A-0 089 497, EP-A-0 195 931, EP-A-0 228 003, EP-A-0 038 127, and DE-A-28 18 100.

10

The optical or visual appearance and the weathering stability are primarily the responsibility of the two topmost coats of the multicoat paint system. Thus it is the basecoat, especially aqueous basecoat, which gives 15 the multicoat paint system its color and/or optical effects such as metallic effects or interference effects, while the clearcoat provides not only scratch resistance and etch resistance, i.e., resistance to damaging environmental substances, but also the 20 appearance qualities, i.e., the gloss, brilliance, and evenness. In this system, aqueous basecoat material and clearcoat material must be very precisely matched to one another in order to produce a system having the desired advantageous profile of properties.

25

Aqueous basecoat materials and the corresponding paint systems which substantially meet these requirements are known from the patents EP-A-0 089 497, EP-A-0 256 540, EP-A-0 260 447, EP-A-0 297 576, WO 96/12747,

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EP-A-0 523 610, EP-A-0 228 003, EP-A-0 397 806,
 EP-A-0 574 417, EP-A-0 531 510, EP-A-0 581 211,
 EP-A-0 708 788, EP-A-0 593 454, DE-A-43 28 092,
 EP-A-0 299 148, EP-A-0 394 737, EP-A-0 590 484,
 5 EP-A-0 234 362, EP-A-0 234 361, EP-A-0 543 817,
 WO 95/14721, EP-A-0 521 928, EP-A-0 522 420,
 EP-A-0 522 419, EP-A-0 649 865, EP-A-0 536 712,
 EP-A-0 596 460, EP-A-0 596 461, EP-A-0 584 818,
 EP-A-0 669 356, EP-A-0 634 431, EP-A-0 678 536,
 10 EP-A-0 354 261, EP-A-0 424 705, WO 97/49745,
 WO 97/49747 or EP-A-0 401 565.

For producing a single-coat or multicoat clearcoat system, use is nowadays made of the customary and known
 15 one-component (1K), two-component (2K), multicomponent (3K, 4K) power or powder slurry clearcoat materials or UV-curable clearcoat materials.

One-component (1K), two-component (2K) or
 20 multicomponent (3K, 4K) clearcoat materials are described, for example, in the patents US-A-5,474,811, US-A-5,356,669, US-A-5,605,965, WO 94/10211, WO 94/10212, WO 94/10213, EP-A-0 594 068, EP-A-0 594 071, EP-A-0 594 142, EP-A-0 604 992,
 25 WO 94/22969, EP-A-0 596 460 or WO 92/22615.

Powder clearcoat materials are known, for example, from the German patent DE-A-42 22 194 or the BASF Lacke +

- 5 -

Farben AG product information leaflet "Pulverlacke"
[powder coating materials], 1990.

Powder slurry coating materials comprise powder
5 coatings in the form of aqueous dispersions. Slurries
of this kind are described, for example, in the US
patent US-A-4,268,542 and the German patent
applications DE-A-195 18 392.4 and DE-A-196 13 547, and
in the German patent application DE-A-198 14 471.7,
10 which was unpublished at the priority date of the
present specification.

UV-curable clearcoat materials are disclosed, for
example, in the patents EP-A-0 540 884, EP-A-0 568 967
15 or US-A-4,675,234.

Each of these clearcoat materials has specific
strengths and weaknesses. Accordingly, these clearcoat
materials produce multicoat systems which satisfy the
20 optical requirements. However, the scratch-resistant
one-component (1K) clearcoats are sometimes not
sufficiently stable to weathering, whereas the
weathering-stable two-component (2K) or multicomponent
(3K, 4K) clearcoats are often not sufficiently scratch-
25 resistant. Some one-component (1K) clearcoats, although
scratch-resistant and stable to weathering, exhibit
surface defects such as shrinkage (wrinkling) in
combination with frequently employed aqueous basecoats.

Powder clearcoats, powder slurry clearcoats, and UV-curable clearcoats, on the other hand, have a not entirely satisfactory intercoat adhesion, without fully solving the problems of scratch resistance or of etch
5 resistance.

EP-A-0 568 967 discloses a process for producing multicoat paint systems, wherein a thermally curable clearcoat film is applied by the wet-on-wet technique
10 to a pigmented basecoat film and then the two films are heat-cured together. Atop the cured clearcoat there is then applied at least one further clearcoat film based on coating materials curable with actinic radiation, which is cured with actinic radiation or thermally and
15 with actinic radiation. This process provides clearcoats with high chemical resistance and optical quality. The scratch resistance, however, is unsatisfactory.

20 EP-A-0 568 967 further discloses a process wherein a coating material curable with actinic radiation is applied to the pigmented basecoat film and cured. Then a further film of the same coating material is applied and is cured using actinic radiation. Although the
25 result is a highly glossy surface without perceptible texture, this clearcoat yellows. Also, the scratch resistance continues to leave something to be desired.

- 7 -

More recently, materials known as sol-gel clearcoats and based on siloxane-containing coating formulations have been developed which are obtained by hydrolysis and condensation of silane compounds. These materials, which are used as coating compositions on plastics, are described, for example, in the German patents DE-A-43 03 570, DE-A-34 07 087, DE-A-40 11 045, DE-A-40 25 215, DE-A-38 28 098, DE-A-40 20 316 or DE-A-41 22 743.

10

Sol-gel clearcoats impart very good scratch resistance to substrates made of plastic, such as spectacle lenses or motorcycle helmet visors, for example. This scratch resistance is not achieved by the above-described, known OEM (original equipment manufacturing) clearcoat materials normally used for the original finishing of vehicles. The automobile industry is now demanding that this improved scratch resistance be transferred to the clearcoats used in the finishing of automobiles, as well. Better protection is intended in particular for those parts of the automobile bodies that are particularly highly stressed, such as hood, bumpers, sills or doors in the door-handle region.

25 Replacing the OEM clearcoat materials or OEM powder slurry clearcoat materials commonly used in automotive finishing by sol-gel clearcoat materials, however, is not immediately possible, since the clearcoats are too brittle for this purpose, for example, or because the

optical properties (appearance) achieved during the attempt to adapt them to the OEM requirements are frequently poor. Furthermore, they cannot be applied at thicknesses > 8 to $10 \mu\text{m}$. Moreover, constituents of the sol-gel clearcoat materials may "strike through" during their drying and/or curing; that is, they are absorbed by the substrate, and, as a result, the clearcoats in question lose hardness. Above all, however, the sol-gel clearcoat materials are too expensive.

10

The economically more favorable use of the sol-gel clearcoat materials as an additional coat over the clearcoats used to date gives rise to adhesion problems within the multicoat clearcoat system, between the clearcoat and the sol-gel coat, these problems arising in particular after stonechipping and on exposure to condensation. In some cases, these problems are exacerbated by virtue of the fact that adhesion between the clearcoat and the substrate is also affected.

20

These problems may be solved to a certain degree by subjecting the clearcoat film that is to be coated with the sol-gel clearcoat material to only partial curing, so that on conjoint curing the sol-gel coating can be anchored chemically, so to speak, on the clearcoat film. However, the second clearcoat film requires a long oven drying time to cure, which is a considerable disadvantage.

15

20 A) at least one binder containing at least two functional groups (a1) which are able to undergo thermal crosslinking reactions with complementary functional groups (b1) in the crosslinking agent (B), and

B) at least one crosslinking agent containing at least two functional groups (b1) which are able to undergo thermal crosslinking reactions with the

- 10 -

complementary functional groups (a1) in the binder
(A),

and also, if desired,

5

C) at least one constituent which is crosslinkable
with actinic radiation,

D) at least one photoinitiator,

10

E) at least one thermal crosslinking initiator,

F) at least one reactive diluent curable with actinic
radiation and/or thermally,

15

G) at least one coatings additive, and/or

H) at least one organic solvent,

20 in which at least one binder (A) contains in
copolymerized form at least one olefinically
unsaturated polysiloxane macromonomer containing on
average per molecule at least 3.0 double bonds.

25 In the text below, the novel coating material curable
thermally and, if desired, with actinic radiation is
referred to as "coating material of the invention".

The invention further provides the novel highly scratch-resistant multicoat clearcoat system KL for a primed or unprimed substrate, which is producible by

- 5 (1) applying at least one clearcoat film I of a coating material I curable thermally and, if desired, with actinic radiation to the surface of the substrate and
 - 10 (1.1) partly or
 - (1.2) fullycuring it, and
- 15 (2) applying a further clearcoat film II of a coating material II curable thermally and, if desired, with actinic radiation to the surface of the clearcoat film(s) I
- 20 (3) and then curing
 - (3.1) the clearcoat films I and II together or
 - (3.2) the clearcoat film II alone,
- 25 thermally and, if desired, with actinic radiation,

wherein the coating material II and/or the coating material I, especially the coating material II, is a coating material of the invention.

The novel highly scratch-resistant multicoat clearcoat system KL is referred to below as the "clearcoat system KL of the invention".

5

The invention further provides the novel process for producing a highly scratch-resistant multicoat clearcoat system KL on a primed or unprimed substrate by

10

- (1) applying at least one clearcoat film I of a coating material I curable thermally and, if desired, with actinic radiation to the surface of the substrate and

15

- (1.1) partly or
 - (1.2) fully

curing it, and

20

- (2) applying a further clearcoat film II of a coating material II curable thermally and, if desired, with actinic radiation to the surface of the clearcoat film(s) I

25

- (3) and then curing

- (3.1) the clearcoat films I and II together or
 - (3.2) the clearcoat film II alone,

thermally and, if desired, with actinic radiation,

wherein the coating material II and/or the coating
5 material I, especially the coating material II, is a
coating material of the invention.

In the text below, the novel process for producing
highly scratch-resistant clearcoat systems KL is
10 referred to as "KL process of the invention".

The invention additionally provides the novel highly
scratch-resistant multicoat color and/or effect paint
system ML for a primed or unprimed substrate, which is
15 producible by

(1) applying at least one color and/or effect basecoat
film III of a pigmented coating material III
curable thermally and, if desired, with actinic
20 radiation to the surface of the substrate, and
drying it without curing,

(2) applying at least one clearcoat film I of a
coating material I curable thermally and, if
25 desired, with actinic radiation to the surface of
the basecoat film III, and

(2.1) partly curing it alone,

- 14 -

(2.2) partly curing it together with the
basecoat film III, or

(2.3) fully curing it together with the
basecoat film III,

5

thermally and, if desired, with actinic radiation,
and

(3) applying a further clearcoat film II of a coating
10 material II curable thermally and, if desired,
with actinic radiation to the surface of the
clearcoat film(s) I,

(4) and then curing
15

(4.1) the clearcoat films I and II and the
basecoat film III together or

(4.2) the clearcoat film II alone,

20 thermally and, if desired, with actinic radiation,

in which the coating material II and/or the coating
material I, especially the coating material II, is a
coating material of the invention.

25

In the text below, the novel multicoat color and/or
effect paint system ML is referred to as "multicoat
paint system ML of the invention".

The invention additionally provides the novel process for producing a highly scratch-resistant multicoat color and/or effect paint system ML on a primed or unprimed substrate by

5

(1) applying at least one color and/or effect basecoat film III of a pigmented coating material III curable thermally and, if desired, with actinic radiation to the surface of the substrate, and
10 drying it without curing,

15

(2) applying at least one clearcoat film I of a coating material I curable thermally and, if desired, with actinic radiation to the surface of the basecoat film III, and

20

(2.1) partly curing it alone,
(2.2) partly curing it together with the basecoat film III, or
(2.3) fully curing it together with the basecoat film III,

thermally and, if desired, with actinic radiation, and

25

(3) applying a further clearcoat film II of a coating material II curable thermally and, if desired, with actinic radiation to the surface of the clearcoat film(s) I,

- 16 -

(4) and then curing

(4.1) the clearcoat films I and II and the
5 basecoat film III together or

(4.2) the clearcoat film II alone,

thermally and, if desired, with actinic radiation,

10 in which the coating material II and/or the coating
material I, especially the coating material II, is a
coating material of the invention.

In the text below, the novel process for producing a
15 highly scratch-resistant multicoat color and/or effect
paint system ML is referred to as the "ML process of
the invention".

The invention relates not least to primed or unprimed
20 substrates coated with at least one clearcoat system KL
of the invention and/or with at least one multicoat
paint system ML of the invention.

In the context of the present invention, the term
25 "thermal curing" denotes the heat-initiated curing of a
film of a coating material for which normally a
separate crosslinking agent is employed. It is commonly
referred to by those in the art as external
crosslinking. Where the crosslinking agents are already

incorporated in the binders, the term "self-crosslinking" is used. In accordance with the invention, external crosslinking is of advantage and is therefore employed with preference.

5

In the context of the present invention, actinic radiation means electron beams or, preferably, UV radiation. Curing by UV radiation is normally initiated by radical or cationic photoinitiators and in terms of
10 its mechanism is a radical or cationic photopolymerization.

Where thermal curing and curing with actinic light are employed together for a coating material, the term
15 "dual cure" is used.

In the light of the prior art it was surprising and unforeseeable for the skilled worker that the complex object on which the invention is based could be
20 achieved by means of the coating material of the invention, the clearcoat system KL of the invention, and the multicoat paint system ML of the invention, and also the KL and ML processes of the invention. A particular surprise is that not only the intercoat
25 adhesion within the clearcoat system KL of the invention but also the adhesion to the basecoat III within the multicoat paint system ML of the invention are improved to an extent far beyond that known. The clearcoat system KL of the invention and the multicoat

paint system ML of the invention have outstanding optical properties, particularly a high level of fullness, high DOI values, high gloss, and no yellowing. In combination with these properties, the clearcoat system KL of the invention and the multicoat paint system ML of the invention are of outstanding weathering stability and chemical stability. Not least, however, they are extraordinarily scratch-resistant.

10 The coating material of the invention comprises as
essential constituent at least one binder (A)
containing in copolymerized form at least one
olefinically unsaturated polysiloxane macromonomer
which has on average per molecule at least 3.0 double
15 bonds.

In accordance with the invention it is of advantage if the polysiloxane macromonomer has on average per molecule at least 4.0, with particular preference 5.0, and in particular 5.5 double bonds. In order to obtain the advantages according to the invention, it is sufficient in the great majority of cases for there to be on average per molecule 10.5, preferably 9.0, with particular preference 8.5, and in particular 8.0 double bonds. Particular advantages are obtained if the polysiloxane macromonomer contains on average per molecule from 5.5 to 6.5, in particular 6.0, double bonds.

5 particular preference from 2 000 to 30 000, and in particular from 2500 to 20 000 daltons.

10 form.

15 alkyl-aryl-, alkyl-cycloalkyl-, cycloalkyl-aryl- or
arylsiloxane resins. Advantageously, the alkyl radicals
contain from 1 to 10, with particular preference from 1
to 5, and in particular from 1 to 3 carbon atoms, the
cycloalkyl radicals contain from 3 to 10, with
20 particular preference from 4 to 8, and in particular
from 5 to 7 carbon atoms, and the aryl radicals contain
from 6 to 12 and, in particular, from 6 to 10 carbon
atoms.

25 Of these radicals, the alkyl radicals are of particular advantage and are therefore used with particular preference. In terms of the preparation of the polysiloxane macromonomers and their technical effects in the binders (A) and in the coating materials of the

invention, methyl radicals prove especially advantageous. They are therefore used with very particular preference.

The above-described polysiloxane macromonomers for inventive use are prepared by the conventional methods of polysiloxane chemistry. The polysiloxane macromonomers for inventive use are, moreover, available on the market and are sold, for example, by Tego Chemie Service GmbH under the trade name Tego® LA-S 517.

The binders (A) for inventive use may contain the polysiloxane macromonomers in copolymerized form in widely varying amounts. Owing to their high functionality of on average more than 3.0 double bonds per molecule, a fraction of up to 15% by weight, preferably up to 10% by weight, with particular preference up to 5% by weight, and in particular up to 2% by weight, based in each case on the binder (A), is sufficient in the great majority of cases to achieve

the technical effects and advantages according to the invention. In this context it proves to be of very particular advantage, in accordance with the invention, that amounts of just at least 0.01% by weight, preferably at least 0.05% by weight, with particular preference at least 0.08% by weight, and in particular at least 0.1% by weight, based in each case on the binder (A), bring about the technical effects and advantages according to the invention.

10

The binders (A) for inventive use contain at least two, particularly at least three, functional groups (a1) which are able to undergo thermal crosslinking reactions with complementary functional groups (b1) in the crosslinking agent (B).

15

Examples of suitable complementary reactive functional groups (a1) and (b1) for use in accordance with the invention, which undergo crosslinking reactions, are assembled in the following overview. In the overview, the variable R stands for an acyclic or cyclic aliphatic radical, an aromatic radical and/or an aromatic-aliphatic (araliphatic) radical; the variables R^1 and R^2 stand for identical or different aliphatic radicals or are linked with one another to form an aliphatic or heteroaliphatic ring.

20

25

**Overview: Examples of complementary functional groups
(a1) and (b2) in**

Binder (A) and crosslinking agent (B)

or

Crosslinking agent (B) and binder (A)

-SH

-C(O)-OH

-NH₂

-C(O)-O-C(O)-

-OH

-NCO

-O-(CO)-NH-(CO)-NH₂

-NH-C(O)-OR

-O-(CO)-NH₂

-CH₂-OH

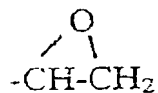
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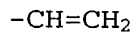
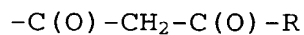
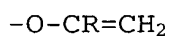
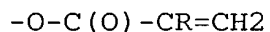
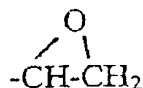
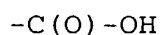
-NH-C(O)-CH(-C(O)OR)₂

-NH-C(O)-CH(-C(O)OR)(-C(O)-R)

-NH-C(O)-NR¹R²

=Si(OR)₂





The selection of the respective complementary groups (a1) and (b2) is guided firstly by the consideration that on storage they must not undergo any unwanted reactions and/or, where appropriate, disrupt or inhibit the curing with actinic radiation, and secondly by the temperature range within which thermal curing is to take place.

10 With a view to thermally sensitive substrates such as plastics, in particular, it is of advantage in accordance with the invention here to choose a temperature range which does not exceed 100°C, particularly 80°C. In view of these boundary conditions, hydroxyl groups and isocyanate groups or
15 carboxyl groups and epoxy groups have proven

Where higher crosslinking temperatures may be employed, for example, from 100°C to 180°C, suitable coating materials of the invention also include one-component systems, in which the functional groups (a1) are preferably thio, amino, hydroxyl, carbamate, allophanate, carboxyl, and/or (meth)acrylate groups, but especially hydroxyl groups, and the functional groups (b1) are preferably anhydride, carboxyl, epoxy, blocked isocyanate, urethane, methylol, methylol ether, siloxane, amino, hydroxyl and/or beta-hydroxyalkylamide groups.

Accordingly, the binders (A) preferred in accordance with the invention are hydroxyl-containing oligomeric or polymeric resins.

25 Examples of suitable binders (A) particularly preferred in accordance with the invention are hydroxyl-containing linear and/or branched and/or block, comb and/or random poly(meth)acrylates or acrylate copolymers, polyesters, alkyds, amino resins,

polyurethanes, acrylated polyurethanes, acrylated polyesters, polylactones, polycarbonates, polyethers, epoxy resin-amine adducts, (meth)acrylated diols, partially hydrolyzed polyvinyl esters or polyureas, of which the acrylate copolymers, the polyesters, the polyurethanes, the polyethers, and the epoxy resin-amine adducts, but especially the acrylate copolymers, are particularly advantageous and are therefore used with particular preference.

10

In the case of binders for aqueous coating materials, the binders include ionic or nonionic groups which ensure solubility in water or dispersibility in water.

15 Particularly preferred acrylate copolymers (A) are preparable by polymerizing (m1) from 10 to 70% by weight, preferably from 20 to 60% by weight, of a hydroxyl-containing ester of acrylic acid or methacrylic acid, or a mixture of such monomers, (m2) from 10 to 70% by weight, preferably from 20 to 60% by weight, of an aliphatic or cycloaliphatic ester of acrylic acid or methacrylic acid preferably having at least 4 carbon atoms in the alcohol residue, which is different than (m1), or of a mixture of such 20 monomers, from 0.01 to 15% by weight, preferably from 0.05 to 10% by weight, of the polysiloxane macromonomer for inventive use, (m3) from 0 to 2% by weight, preferably from 0 to 1% by weight, of an ethylenically unsaturated carboxylic acid or of a mixture of 25

ethylenically unsaturated carboxylic acids, and (m4) from 0 to 30% by weight, preferably from 0 to 20% by weight, of an ethylenically unsaturated monomer different than (m1), (m2), (m3), or of a mixture of
 5 such monomers, to give a polyacrylate resin having an acid number of from 0 to 15, preferably from 0 to 8, a hydroxyl number of from 80 to 140, preferably from 80 to 120, and a number-average molecular weight of from 1500 to 10 000, preferably from 2000 to 5000, the sum
 10 of the weight fractions of components (m1), (m2), (m3), and (m4) always giving 100% by weight.

The acrylate copolymers (A) used with preference may be prepared by widely and well-known polymerization
 15 techniques in bulk, solution or emulsion. Polymerization techniques for preparing polyacrylate resins are widely known and have been much described (cf. e.g.: Houben Weyl, Methoden der organischen Chemie, 4th edition, volume 14/1, page 24 to 255
 20 (1961)).

Further examples of suitable (co)polymerization techniques for preparing the acrylate copolymers (A) are described in the patents DE-A-197 09 465,
 25 DE-C-197 09 476, DE-A-28 48 906, DE-A-195 24 182, EP-A-0 554 783, WO 95/27742, DE-A-38 41 540 or WO 82/02387.

peripheral direction. These vortices, called Taylor
vortices, are rotationally symmetric and have a
diameter which is approximately the same size as the
gap width. Two adjacent vortices form a vortex pair or
5 vortex cell.

The basis for this behavior is the fact that, in the
course of rotation of the inner cylinder with the outer
cylinder at rest, the fluid particles that are near to
10 the inner cylinder are subject to a greater centrifugal
force than those at a greater distance from the inner
cylinder. This difference in the acting centrifugal
forces displaces the fluid particles from the inner to
the outer cylinder. The viscosity force acts counter to
15 the centrifugal force, since for the motion of the
fluid particles it is necessary to overcome the
friction. If there is an increase in the rotary speed,
there is also an increase in the centrifugal force. The
Taylor vortices are formed when the centrifugal force
20 exceeds the stabilizing viscosity force.

In the case of Taylor flow with a low axial flow, each
vortex pair passes through the gap, with only a low
level of mass transfer occurring between adjacent
25 vortex pairs. Mixing within such vortex pairs is very
high, whereas axial mixing beyond the pair boundaries
is very low. A vortex pair may therefore be regarded as
a stirred tank in which there is thorough mixing.
Consequently, the flow system behaves as an ideal flow

Of particular advantage in this context are Taylor
5 reactors having an external reactor wall located within
which there is a concentrically or eccentrically
disposed rotor, a reactor floor and a reactor lid,
which together define the annular reactor volume, at
least one means for metered addition of reactants, and
10 a means for the discharge of product, where the reactor
wall and/or the rotor are or is geometrically designed
in such a way that the conditions for Taylor flow are
met over substantially the entire reactor length in the
reactor volume, i.e., in such a way that the annular
15 gap widens in the direction of flow therethrough.

The acrylate copolymers (A) used are preferably prepared by means of the solution polymerization process. In this process, normally an organic solvent or solvent mixture is introduced as the initial charge and is heated to boiling. The monomer mixture to be polymerized, together with one or more polymerization initiators, are then added continuously to this organic solvent or solvent mixture. The polymerization takes place at temperatures between 100 and 160°C, preferably between 130 and 150°C. As copolymerization initiators it is preferred to use initiators which form free radicals. The strength and amount of initiator are customarily chosen in such a way that the supply of

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of the hydroxyl number. It can be controlled by the amount of monomer (ml) used.

As monomers (ml) it is possible in principle to use any
 5 hydroxyl-containing ester of acrylic acid or methacrylic acid, or a mixture of such monomers. Examples include the following: hydroxyalkyl esters of acrylic acid, such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, for
 10 example, especially 4-hydroxybutyl acrylate; hydroxyalkyl esters of methacrylic acid, such as hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, for example, especially 4-hydroxybutyl methacrylate; and reaction products of
 15 cyclic esters, such as epsilon-caprolactone, for example, and hydroxyalkyl esters of acrylic acid and/or methacrylic acid.

The composition of the monomers (ml) is preferably
 20 selected such that polymerization of the monomers (ml) alone gives a polyacrylate resin having a glass transition temperature of from -50 to +70°C, preferably from -30 to +50°C. The glass transition temperature may be calculated approximately by the skilled worker with
 25 the aid of the formula

$$n = x$$

$$1/T_G = \sum W_n/T_{Gn}$$

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$$n = 1$$

- T_G = glass transition temperature of the polymer
 X = number of different polymerized monomers
5 W_n = weight fraction of the n th monomer
 T_{Gn} = glass transition temperature of the homopolymer
of the n th monomer.

As monomer (m2) it is possible in principle to use any
10 aliphatic or cycloaliphatic ester of acrylic acid or
methacrylic acid having at least 4 carbon atoms in the
alcohol residue which is different than (m1), or a
mixture of such monomers. Examples include the
following: aliphatic esters of acrylic and methacrylic
15 acid having from 4 to 20 carbon atoms in the alcohol
residue, such as n-butyl, isobutyl, tert-butyl,
2-ethylhexyl, stearyl, and lauryl acrylate and
methacrylate, for example, and also cycloaliphatic
esters of acrylic and methacrylic acid, such as
20 cyclohexyl acrylate and cyclohexyl methacrylate, for
example. The composition of the monomers (m2) is
preferably selected so that polymerization of the
monomers (m2) alone gives a polyacrylate resin having a
glass transition temperature of from 10 to 100°C,
25 preferably from 20 to 60°C.

As monomer (m3) it is possible in principle to use any
ethylenically unsaturated carboxylic acid or a mixture
of ethylenically unsaturated carboxylic acids. As

monomer (m3) it is preferred to use acrylic acid and/or methacrylic acid.

As monomer (m4) it is possible in principle to use any
5 ethylenically unsaturated monomer that is different than (m1), (m2), and (m3), or a mixture of such monomers. Examples of monomers which may be used as component (m4) include the following: vinylaromatic hydrocarbons, such as styrene, alpha-alkylstyrene and
10 vinyltoluene, amides of acrylic acid and methacrylic acid, such as methacrylamide and acrylamide, nitriles of methacrylic acid and acrylic acid, for example; vinyl ethers and vinyl esters or polysiloxane macromonomers, such as are described in the patents
15 DE-A-38 07 571, DE-A-37 06 095, EP-B-0 358 153, US-A 4,754,014, DE-A 44 21 823 or WO 92/22615. As monomers (m4) it is preferred to use vinylaromatic hydrocarbons, especially styrene. The composition of the monomers (m4) is preferably selected so that polymerization of
20 the monomers (m4) alone gives a resin having a glass transition temperature of from 70 to 120°C, preferably from 80 to 100°C.

In the coating material of the invention the binders
25 (A) are present advantageously in an amount of from 5 to 95% by weight, with particular preference from 7 to 70% by weight, and in particular from 10 to 50% by weight, based in each case on the overall solids content of the coating material of the invention.

The coating material of the invention further comprises at least one crosslinking agent (B) which contains at least two, in particular three, of the complementary functional groups (b1) described in detail above.

Where the coating material of the invention is a two-component or multicomponent system, polyisocyanates and/or polyepoxides, but especially polyisocyanates, are used as crosslinking agents (B).

Examples of suitable polyisocyanates (B) are organic polyisocyanates, especially what are known as pink polyisocyanates, containing aliphatically, cycloaliphatically, araliphatically and/or aromatically bonded, free isocyanate groups. Preference is given to using polyisocyanates having from 2 to 5 isocyanate groups per molecule and having viscosities of from 100 to 10 000, preferably from 100 to 5 000, and in particular from 100 to 2 000 mPas (at 23°C). If desired, small amounts of organic solvent, preferably from 1 to 25% by weight based on straight polyisocyanate, may be added to the polyisocyanates in order thus to improve the ease of incorporation of the isocyanate and, where appropriate, to lower the viscosity of the polyisocyanate to a level within the abovementioned ranges. Examples of suitable solvent additives to the polyisocyanates are epoxyethyl propionate, amyl methyl ketone or butyl acetate.

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Furthermore, the polyisocyanates (B) may have been hydrophilically or hydrophobically modified in a conventional way.

5 Examples of suitable polyisocyanates (B) are described, for example, in "Methoden der organischen Chemie", Houben-Weyl, volume 14/2, 4th edition, Georg Thieme Verlag, Stuttgart 1963, page 61 to 70, and by W. Siefken, Liebigs Annalen der Chemie, volume 562,
10 pages 75 to 136. Also suitable, for example, are the polyurethane prepolymers containing isocyanate groups which can be prepared by reacting polyols with an excess of polyisocyanates and which are preferably of low viscosity.

15

Further examples of suitable polyisocyanates (B) are polyisocyanates containing isocyanurate, biuret, allophanate, iminooxadiazinedone, urethane, urea and/or uretdione groups. Polyisocyanates containing urethane
20 groups, for example, are obtained by reacting some of the isocyanate groups with polyols, such as trimethylolpropane and glycerol, for example. Preference is given to using aliphatic or cycloaliphatic polyisocyanates, especially hexamethylene
25 diisocyanate, dimerized and trimerized hexamethylene diisocyanate, isophorone diisocyanate, 2-isocyanatopropylcyclohexyl isocyanate, dicyclohexylmethane 2,4'-diisocyanate, dicyclohexylmethane 4,4'-diisocyanate or 1,3-bis(isocyanatomethyl)cyclohexane (BIC), diiso-

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cyanates derived from dimer fatty acids, as sold under the commercial designation DDI 1410 by Henkel, 1,8-diisocyanato-4-isocyanatomethyloctane, 1,7-diisocyanato-4-isocyanatomethylheptane or 1-isocyanato-2-(3-isocyanatopropyl)cyclohexane, or mixtures of these polyisocyanates.

Examples of suitable polyepoxides (B) are all known aliphatic and/or cycloaliphatic and/or aromatic polyepoxides, based for example on bisphenol A or bisphenol F. Examples of suitable polyepoxides also include the polyepoxides available commercially under the designations Epikote® from Shell, Denacol® from Nagase Chemicals Ltd, Japan, such as, for example, Denacol EX-411 (pentaerythritol polyglycidyl ether), Denacol EX-321 (trimethylolpropane polyglycidyl ether), Denacol EX-512 (polyglycerol polyglycidyl ether), and Denacol EX-521 (polyglycerol polyglycidyl ether).

In the case of the one-component systems, crosslinking agents (B) are used which react at relatively high temperatures with the functional groups of the binders, in order to build up a three-dimensional network. Of course, such crosslinking agents (B) may be used as well in minor amounts in the multicomponent systems. In the context of the present invention, "minor amounts" means a fraction which does not disrupt, let alone prevent entirely, the main crosslinking reaction.

Examples of suitable crosslinking agents (B) of this kind are blocked polyisocyanates. Examples of suitable polyisocyanates are those described above.

5 Examples of suitable blocking agents are the blocking agents known from the US patent US-A-4,444,954, such as

i) phenols such as phenol, cresol, xyleneol,
nitrophenol, chlorophenol, ethylphenol, t-butyl-
10 phenol, hydroxybenzoic acid, esters of this acid
or 2,5-di-t-butyl-4-hydroxytoluene;

ii) lactams, such as ϵ -caprolactam, δ -valerolactam,
15 γ -butyrolactam or β -propiolactam;

iii) active methylenic compounds, such as diethyl
malonate, dimethyl malonate, ethyl acetoacetate,
methyl acetoacetate or acetylacetone;

20 iv) alcohols such as methanol, ethanol, n-propanol,
isopropanol, n-butanol, isobutanol, t-butanol,
n-amyl alcohol, t-amyl alcohol, lauryl alcohol,
ethylene glycol monomethyl ether, ethylene glycol
monoethyl ether, ethylene glycol monopropyl ether,
25 ethylene glycol monobutyl ether, diethylene glycol
monomethyl ether, diethylene glycol monoethyl
ether, propylene glycol monomethyl ether,
methoxymethanol, glycolic acid, glycolic esters,
lactic acid, lactic esters, methylolurea,

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methylolmelamine, diacetone alcohol,
ethylenechlorohydrin, ethylenebromohydrin, 1,3-
dichloro-2-propanol, 1,4-cyclohexyldimethanol or
acetocyanohydrin;

5

v) mercaptans such as butyl mercaptan, hexyl
mercaptan, t-butyl mercaptan, t-dodecyl mercaptan,
2-mercaptobenzothiazole, thiophenol, methylthio-
phenol or ethylthiophenol;

10

vi) acid amides such as acetoanilide, aceto-
anisidinamide, acrylamide, methacrylamide,
acetamide, stearamide or benzamide;

15 vii) imides such as succinimide, phthalimide or
maleimide;

viii) amines such as diphenylamine, phenylnaphthylamine,
xylidine, N-phenylxylidine, carbazole, aniline,
20 naphthylamine, butylamine, dibutylamine or
butylphenylamine;

ix) imidazoles such as imidazole or 2-ethylimidazole;

25 x) ureas such as urea, thiourea, ethyleneurea,
ethylenethiourea or 1,3-diphenylurea;

xi) carbamates such as phenyl N-phenylcarbamate or
2-oxazolidone;

xii) imines such as ethyleneimine;

5 xiii) oximes such as acetone oxime, formaldoxime,
 acetaldoxime, acetoxime, methyl ethyl ketoxime,
 diisobutyl ketoxime, diacetyl monoxime, benzo-
 phenone oxime or chlorohexanone oximes;

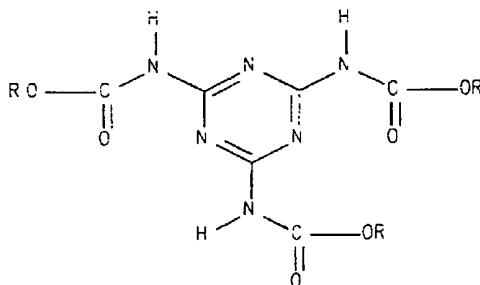
10 xiv) salts of sulfurous acid such as sodium bisulfite
 or potassium bisulfite;

 xv) hydroxamic esters such as benzyl methacrylo-
 hydroxamate (BMH) or allyl methacrylohydroxamate;
 or

15 xvi) substituted pyrazoles, ketoximes, imidazoles or
 triazoles; and also

 mixtures of these blocking agents, especially
 20 dimethylpyrazole and triazoles, malonic esters and
 acetoacetic esters, or dimethylpyrazole and
 succinimide.

 As crosslinking agents (B) it is also possible to use
 25 tris(alkoxycarbonylamino)triazines (TACT) of the
 formula



Examples of suitable tris(alkoxycarbonylamino)triazines are described in the patents US-A-4,939,213, 5 US-A-5,084,541 or EP-A-0 624 577. Use is made in particular of the tris(methoxy-, tris(butoxy- and/or tris(2-ethylhexoxycarbonylamino)triazines.

Of advantage are the methyl butyl mixed esters, the 10 butyl 2-ethylhexyl mixed esters and the butyl esters. They have the advantage over the straight methyl ester of better solubility in polymer melts, and also have less of a tendency to crystallize.

15 In particular it is possible to use amino resins, examples being melamine resins, as crosslinking agents (B). In this context it is possible to use any amino resin suitable for transparent topcoat materials or clearcoat materials, or a mixture of such amino resins. 20 Particularly suitable are the customary and known amino resins some of whose methylol and/or methoxymethyl groups have been defunctionalized by means of carbamate or allophanate groups. Crosslinking agents of this kind are described in the patents US-A-4 710 542 and 25 EP-B-0 245 700 and also in the article by B. Singh and

coworkers, "Carbamylmethylated Melamines, Novel Crosslinkers for the Coatings Industry", in Advanced Organic Coatings Science and Technology Series, 1991, volume 13, pages 193 to 207.

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Further examples of suitable crosslinking agents (B) are beta-hydroxyalkylamides such as N,N,N',N'-tetrakis(2-hydroxyethyl)adipamide or N,N,N',N'-tetrakis(2-hydroxypropyl)adipamide.

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Further examples of suitable crosslinking agents (B) are siloxanes, especially siloxanes containing at least one trialkoxy- or dialkoxysilane group.

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Further examples of suitable crosslinking agents (B) are polyanhydrides, especially polysuccinic anhydride.

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The amount of the crosslinking agent (B) in the coating material of the invention may vary widely and is guided in particular, firstly, by the functionality of the crosslinking agents (B) and, secondly, by the number of crosslinking functional groups (a1) present in the binder (A) and also by the target crosslinking density. The skilled worker is therefore able to determine the amount of the crosslinking agent (B) on the basis of his or her general art knowledge, where appropriate with the assistance of simple rangefinding tests. Advantageously, the crosslinking agent (B) is present in the coating material of the invention in an amount

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of from 5 to 60% by weight, with particular preference from 10 to 50% by weight, and in particular from 15 to 45% by weight, based in each case on the overall solids content of the coating material of the invention. It is
 5 further advisable here to choose the amounts of crosslinking agent (B) and binder (A) such that in the coating material of the invention the ratio of functional groups (b1) in the crosslinking agent (B) and functional groups (a1) in the binder (A) is between
 10 2:1 to 1:2, preferably 1.5:1 to 1:1.5, with particular preference 1.2:1 to 1:1.2, and in particular 1.1:1 to 1:1.1.

If the coating material of the invention is to be
 15 curable not only thermally but also with actinic radiation, especially UV radiation and/or electron beams (dual cure), it includes at least one constituent (C) which is curable with actinic radiation.

20 Suitable constituents (C) include in principle all oligomeric and polymeric compounds which are curable with actinic radiation, especially UV radiation and/or electron beams, and which are customarily used in the field of UV-curable or electron beam-curable coating
 25 materials.

It is advantageous to use radiation-curable binders as constituents (C). Examples of suitable radiation-curable binders (C) are (meth)acryloyl-functional,

(meth)acrylic copolymers, polyether acrylates, polyester acrylates, unsaturated polyesters, epoxy acrylates, urethane acrylates, amino acrylates, melamine acrylates, silicone acrylates, and the
5 corresponding methacrylates. It is preferred to use binders (C) which are free from aromatic structural units. Preference is therefore given to using urethane (meth)acrylates and/or polyester (meth)acrylates, with particular preference aliphatic urethane acrylates.

10

The coating material of the invention may further comprise at least one photoinitiator (D). If the coating material or the clearcoat film is to be crosslinked additionally with UV radiation, the use of
15 a photoinitiator (B) is generally necessary. Where it is used, it is present in the coating material of the invention preferably in fractions of from 0.1 to 10% by weight, with particular preference from 1 to 8% by weight, and in particular from 2 to 6% by weight, based
20 in each case on the overall solids content of the coating material of the invention.

Examples of suitable photoinitiators (D) are those of the Norrish II type, whose mechanism of action is based
25 on an intramolecular variant of the hydrogen abstraction reactions such as occur diversely in photochemical reactions (reference may be made here, by way of example, to Römpp Chemie Lexikon, 9th expanded and revised edition, Georg Thieme Verlag Stuttgart, Vol. 4,

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based in each case on the overall solids content of the coating material of the invention.

Moreover, the coating material may comprise at least
5 one reactive diluent (F) curable thermally and/or with actinic radiation.

Examples of suitable thermally crosslinkable reactive
diluent (F) are branched, cyclic and/or acyclic C₉-C₁₆
10 alkanes functionalized with at least two hydroxyl groups, preferably dialkyloctanediols, especially the positionally isomeric diethyloctanediols.

Further examples of suitable thermally crosslinkable
15 reactive diluent (F) are oligomeric polyols obtainable from oligomeric intermediates themselves obtained by metathesis reactions from acyclic monoolefins and cyclic monoolefins, by hydroformylation and subsequent hydrogenation; examples of suitable cyclic monoolefins
20 are cyclobutene, cyclopentene, cyclohexene, cyclo-octene, cycloheptene, norbornene or 7-oxanorbornene; examples of suitable acyclic monoolefins are present in hydrocarbon mixtures obtained in petroleum processing by cracking (C₅ cut).

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Examples of suitable oligomeric polyols for use in accordance with the invention have a hydroxyl number (OHN) of from 200 to 450, a number-average molecular

glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol monobutyl ether, trimethylolpropane, ethyl 2-hydroxypropionate and 3-methyl-3-methoxybutanol, and also derivatives based on propylene
5 glycol, e.g., isopropoxypropanol.

Examples of reactive diluents (F) used that may be crosslinked with actinic radiation are the above-detailed polysiloxane macromonomers for inventive use,
10 (meth)acrylic acid and other esters thereof, maleic acid and its esters, including monoesters, vinyl acetate, vinyl ethers, vinylureas, and the like. Examples that may be mentioned include alkylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate,
15 1,3-butanediol di(meth)acrylate, vinyl (meth)acrylate, allyl (meth)acrylate, glycerol tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, trimethylolpropane di(meth)acrylate, styrene, vinyltoluene, divinylbenzene, pentaerythritol tri(meth)acrylate,
20 pentaerythritol tetra(meth)acrylate, dipropylene glycol di(meth)acrylate, hexanediol di(meth)acrylate, ethoxyethoxyethyl acrylate, N-vinylpyrrolidone, phenoxyethyl acrylate, dimethylaminoethyl acrylate, hydroxyethyl (meth)acrylate, butoxyethyl acrylate,
25 isobornyl (meth)acrylate, dimethylacrylamide, and dicyclopentyl acrylate, and the long-chain linear diacrylates described in EP-A-0 250 631 and having a molecular weight of from 400 to 4 000, preferably from 600 to 2 500. The two acrylate groups may, for example,

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be separated by a polyoxybutylene structure. Further candidates for use are 1,12-dodecyl diacrylate and the reaction product of 2 moles of acrylic acid with one mole of a dimeric fatty alcohol having generally 36 carbon atoms. Mixtures of the abovementioned monomers are also suitable.

Preferred for use as reactive diluents (F) are mono- and/or diacrylates, such as isobornyl acrylate, hexanediol diacrylate, tripropylene glycol diacrylate, Laromer® 8887 from BASF AG, and Actilane® 423 from Akcros Chemicals Ltd., UK, for example. Particular preference is given to the use of isobornyl acrylate, hexanediol diacrylate, and tripropylene glycol diacrylate.

Where used, the reactive diluents (F) are employed in an amount of preferably from 2 to 70%, with particular preference from 10 to 65%, and in particular from 15 to 50%, by weight, based in each case on the overall solids content of the coating material of the invention.

The coating material may further comprise at least one customary and known coatings additive (G) in effective amounts, i.e., in amounts of preferably up to 40% by weight, with particular preference up to 30% by weight, and in particular up to 20% by weight, based in each case on the overall solids content of the coating

- flattening agents.

Nonaqueous coating materials of the invention may contain from 20 to 70% by weight, preferably from 40 to 60% by weight (based on the ready-to-apply coating material), of organic solvents (H), such as aliphatic, aromatic and/or cycloaliphatic hydrocarbons, alkyl esters of acetic acid or propionic acid, alkanols, ketones, glycol ethers and/or glycol ether esters, for example.

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Accordingly, given the appropriate choice of its above-described constituents (A) and (B) and also, where appropriate, (C), (D), (E), (F), (G) and/or (H), it may be in the form of a liquid coating material which is
 5 substantially free from organic solvents and/or water (100% system).

Alternatively, the coating material may be a solution or dispersion of the above-described constituents in
 10 organic solvents (H) and/or water. It is a further advantage of the coating material of the invention that in this case solids contents of up to more than 80% by weight, based on the coating material, can be set.

15 Furthermore, given an appropriate choice of its above-described constituents, the coating material of the invention may be a powder clearcoat material. For this purpose the constituent (B) may be in microencapsulated form if it is a polyisocyanate. This powder clearcoat
 20 powder may then, if desired, be dispersed in water to give a powder slurry clearcoat material.

The coating material of the invention may be a two-component or multicomponent system in which at least
 25 constituent (B) is stored separately from the other constituents and is added to them only shortly before use. In this case the coating material of the invention may also be aqueous, with constituent (B) being present preferably in a component comprising a solvent (H).

Additionally, the coating material of the invention may be part of a so-called mixer system or modular system, as described, for example, in the patents
5 DE-A-41 10 520, EP-A-0 608 773, EP-A-0 614 951 or EP-A-0 471 972.

The preparation of the coating material of the invention from its constituents (A) and (B) and also,
10 where appropriate, (C), (D), (E), (F), (G) and/or (H) has no special features but instead takes place in a conventional and known manner by mixing the constituents in suitable mixing units such as stirred tanks, dissolvers or extruders in accordance with the
15 processes which are suitable for preparing the respective coating materials, these processes being as described, for example, in the patents set out at the outset.

20 The coating material of the invention serves for producing the clearcoat systems KL and multicoat paint systems ML of the invention on primed or unprimed substrates.

25 Suitable substrates include all surfaces to be coated that are not damaged by curing of the coating systems present thereon using heat and, if desired, actinic radiation; examples include metals, plastics, wood, ceramic, stone, textile, fiber composites, leather,

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glass, glass fibers, glass wool and rock wool, mineral-bound and resin-bound building materials, such as plasterboard panels and cement slabs or roof shingles. Accordingly, the clearcoat system KL of the invention
5 is also suitable for applications outside of automotive finishing, especially for the coating of furniture and for industrial coating, including coil coating and container coating. In the context of industrial coatings it is suitable for coating virtually all parts
10 for private or industrial use such as radiators, domestic appliances, small metal parts, hub caps or wheel rims. In particular, the clearcoat system KL of the invention is suitable as a coating over basecoats, preferably in the automobile industry. It is
15 particularly suitable as a clearcoat over aqueous basecoats based on polyesters, polyurethane resins, and amino resins, particularly as part of the multicoat paint system ML of the invention.

20 Using the clearcoat system KL of the invention or the multicoat paint system ML of the invention it is also possible in particular to coat primed or unprimed plastics such as, for example, ABS, AMMA, ASA, CA, CAB, EP, UF, CF, MF, MPF, PF, PAN, PA, PE, HDPE, LDPE,
25 LLDPE, UHMWPE, PET, PMMA, PP, PS, SB, PUR, PVC, RF, SAN, PBT, PPE, POM, PUR-RIM, SMC, BMC, PP-EPDM, and UP (abbreviations according to DIN 7728T1). The plastics to be coated may of course also be polymer blends, modified plastics or fiber-reinforced plastics. It is

75 μm , with particular preference from 20 to 55 μm , and in particular from 20 to 35 μm .

The application of the coating material I for the purpose of producing the clearcoat film I may take place by any customary application methods, such as spraying, knife coating, brushing, flow coating, dipping or rolling, for example. It is preferred to employ spray application methods, such as compressed air spraying, airless spraying, high speed rotation, electrostatic spray application (ESTA), for example, alone or in conjunction with hot spray application such as hot air spraying, for example. The applications may be carried out at temperatures of max. 70 to 80° Celsius, so that suitable application viscosities are achieved without the short period of thermal stress being accompanied by any change in or damage to the coating material I or its overspray, which may be intended for reprocessing. For instance, hot spraying may be configured in such a way that the coating material I is heated only very shortly in or shortly before the spray nozzle.

The spray booth used for application may be operated, for example, with an optionally thermostatable circulation system which is operated with a suitable absorption medium for the overspray, an example being the coating material I itself.

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Where the coating material I is also curable with actinic radiation, the application is carried out under illumination with visible light having a wavelength of more than 550 nm or in the absence of light. This prevents material change or damage to the coating material I and to the overspray.

The application methods described above can of course also be employed for producing the clearcoat film II or the basecoat film III and also any further coating films as part of the KL and ML processes of the invention.

In accordance with the invention, the clearcoat film I, following its application, is partly or fully cured.

As far as the method is concerned, the partial curing is no different from a customary full curing of a coating film. In this case, crosslinking only takes place for a sufficient time that the clearcoat film I firstly has a dimensional stability which is sufficient for the purposes of the KL or ML processes of the invention and secondly contains a sufficient amount of the above-described crosslinkable functional groups (a1) and (b2) (complementary functional groups) for the postcrosslinking and for the intercoat adhesion. The extent of partial curing may therefore vary widely and is guided by the requirements of the particular case in hand. It may, however, be determined by the skilled

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worker on the basis of his or her general art knowledge and/or on the basis of simple preliminary tests. Preferably from 0.5 to 99.5 mol%, with particular preference from 1 to 99 mol%, with very particular
5 preference from 2 to 90 mol%, and in particular from 3 to 80 mol% of the crosslinkable functional groups present in the coating material I are reacted. It is very particularly preferred if, following its partial curing, the clearcoat film I is still tacky.

10

However, it is also possible for the clearcoat film(s) I to be fully cured. Subsequently, the outer surface of the clearcoat(s) I may be roughened or abraded in order to improve intercoat adhesion, prior to the application
15 of the clearcoat film II. Suitable in this context are the customary and known roughening methods such as abrading with sandpaper or steel wool or files or brushes. However, it is a particular advantage of the KL and ML processes of the invention that abrading of
20 the clearcoat I is generally unnecessary.

In accordance with the invention, the clearcoat film I may be partially or fully cured thermally or both thermally and with actinic radiation.

25

Curing may take place after a certain resting time. This time may have a duration of from 30 s to 2 h, preferably from 1 min to 1 h, and in particular from 1 min to 30 min. The resting time serves, for example,

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also of advantage for economic reasons if the clearcoat film I is the thicker of the two films.

5 The above-described clearcoat systems KL of the invention, produced preferably by means of the KL process of the invention, may also be part of the multicoat paint systems ML of the invention. These systems are advantageously produced by means of the ML process of the invention.

10

For this purpose, in the first process step the clearcoat film(s) I is or are applied not to the primed or unprimed substrates but instead to at least one color and/or effect basecoat film III which is present
15 on said substrates and is produced from a pigmented coating material III which is curable thermally and, if desired, with actinic radiation.

In accordance with the invention it is of advantage to
20 apply the clearcoat film(s) I by the wet-on-wet process to the dried or flashed-off, but uncured basecoat film III and to cure it (them) either partly and alone, partly and together with the basecoat III, or fully together with the basecoat III, thermally and, if
25 desired, with actinic radiation. Where full curing is carried out, the outer surface of the clearcoat film(s) I may be abraded as described above before the clearcoat film II is applied.

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III, following their complete curing, advantageously have a dry film thickness of from 5 to 25 μm , with particular preference from 10 to 20 μm , and in particular from 12 to 18 μm .

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It is, however, also possible to use the pigmented powder coating material known from the European patent EP-A-0 844 286 which is curable thermally and with actinic radiation. It comprises a saturated binder and
10 a second resin, copolymerizable therewith, and also a photoinitiator and a thermal initiator, and is therefore curable thermally and with actinic radiation. The powder basecoat film may be cured on the surface with UV light and cured thermally in the regions close
15 to the substrate.

The clearcoat system KL of the invention exhibits outstanding optical, mechanical, and chemical properties. Thus, it is free from any surface defects
20 such as shrinkage (wrinkling). It is of outstanding transparency and scratch resistance. Delamination owing to deficient intercoat adhesion is not observed. The etch resistance is outstanding. Accordingly, the coating material for inventive use is outstandingly
25 suitable for finishing all conventional clearcoat systems without the need for extensive refitting of the coating lines at the customer's facility. This constitutes a further particular advantage of the multicoat paint systems ML of the invention. The latter

possess, in particular, outstanding color brilliance and/or an outstanding accentuation of the optical effects such as metallic effects, pearlescent effects or flop effects.

5

Examples and Comparative Experiments

Preparation Examples 1 to 6

- 10 1. **The preparation of a polyacrylate (A) which can be used inventively**

A laboratory reactor having a useful volume of 4 l, equipped with a stirrer, two dropping funnels for the monomer mixture and initiator solution, respectively, a nitrogen inlet tube, thermometer, and reflux condenser, was charged with 640.6 g of an aromatic hydrocarbons fraction having a boiling range of 158-172°C. The solvent was heated to 140°C. After 140°C had been reached, a monomer mixture of 597 g of ethylhexyl acrylate, 173.2 g of hydroxyethyl methacrylate, 128.4 g of styrene, 385.2 g of 4-hydroxybutyl acrylate and 3.2 g of a hexaacrylate-functional polysiloxane macromonomer (methylsiloxane resin Tego® LA-S 517 from Tego Chemie Service GmbH; active substance content: 60% by weight) was metered into the reactor at a uniform rate over the course of 4 hours and an initiator solution of 25.6 g of t-butyl perethylhexanoate in 50 g of the aromatic solvent described was metered into the

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reactor at a uniform rate over the course of 4.5 hours. The metered additions of the monomer mixture and the initiator solution were commenced simultaneously. After the end of the metered addition of initiator, the
5 reaction mixture was held at 140°C for a further two hours and then cooled. The resulting polymer solution had a solids content of 65%, determined in a forced air oven at 130°C for 1 h.

10 **2. The preparation of a conventional polyacrylate (A)**

Preparation Example 1 was repeated but without using any polysiloxane macromonomer for inventive use.

15 **3. The preparation of a polyacrylate as grinding resin**

A laboratory reactor having a useful volume of 4 l, equipped with a stirrer, two dropping funnels for the
20 monomer mixture and initiator solution, respectively, a nitrogen inlet tube, thermometer, and reflux condenser, was charged with 720 g of an aromatic hydrocarbons fraction having a boiling range of 158-172°C. The solvent was heated to 140°C. After 140°C had been
25 reached, a monomer mixture of 450 g of 2-ethylhexyl methacrylate, 180 g of n-butyl methacrylate, 210 g of styrene, 180 g of hydroxyethyl acrylate, 450 g of 4-hydroxybutyl acrylate and 30 g of acrylic acid was metered into the reactor at a uniform rate over the

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course of 4 hours and an initiator solution of 150 g of t-butyl perethylhexanoate in 90 g of the aromatic solvent described was metered into the reactor at a uniform rate over the course of 4.5 hours. The metered
 5 additions of the monomer mixture and the initiator solution were commenced simultaneously. After the end of the metered addition of initiator, the reaction mixture was held at 140°C for a further two hours and then cooled. The resulting polymer solution had a
 10 solids content of 65%, determined in a forced air oven at 130°C for 1 h, an acid number of 15 and a viscosity of 3 dPas (measured on a 60% dilution of the polymer solution in the aromatic solvent described, using an ICI cone and plate viscometer at 23°C).

15

4. The preparation of a thixotroping paste

A stirred laboratory mill from Vollrath was charged with 800 g of millbase, consisting of 323.2 g of the
 20 polyacrylate from Preparation Example 3, 187.2 g of butanol, 200.8 g of xylene and 88.8 g of Aerosil® 812 (Degussa AG, Hanau), together with 1100 g of quartz sand (grain size 0.7-1 mm), and this composition was dispersed with water cooling for 30 minutes.

25

5. The preparation of a crosslinking agent (B)

A 4 l stainless steel reactor was charged with 40 parts by weight of Basonat® HI 190 B/S (isocyanurate based on

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hexamethylene diisocyanate from BASF Aktiengesellschaft) and 16.4 parts by weight of solvent naphtha, and this initial charge was heated to 50°C. Over the course of 4 hours, 26.27 parts by weight of diethyl
 5 malonate, 6.5 parts by weight of ethyl acetoacetate and 0.3 part by weight of catalyst solution (sodium ethylhexanoate) were metered in at a uniform rate. Thereafter, the temperature was raised to 70°C. When an isocyanate equivalent weight of from 5 900 to 6 800 had
 10 been reached, 1.03 parts by weight of 1,4-cyclohexyldimethanol were added with stirring at 70°C over the course of 30 minutes. When an isocyanate equivalent weight of • 13 000 had been reached, 5 parts by weight of n-butanol were added. The temperature was lowered to
 15 50°C and the resulting blocked polyisocyanate was diluted with n-butanol to a theoretical solids content of 68% by weight.

**6. The preparation of a further conventional
 20 polyacrylate (A)**

A laboratory reactor having a useful volume of 4 l, equipped with a stirrer, two dropping funnels for the monomer mixture and initiator solution, respectively, a
 25 nitrogen inlet tube, thermometer, and reflux condenser, was charged with 720 g of an aromatic hydrocarbons fraction having a boiling range of 158-172°C. The solvent was heated to 140°C. After 140°C had been reached, a monomer mixture of 427.5 g of n-butyl

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acrylate, 180 g of n-butyl methacrylate, 450 g of
styrene, 255 g of hydroxyethyl acrylate, 165 g of
4-hydroxybutyl acrylate and 22.5 g of acrylic acid was
metered into the reactor at a uniform rate over the
5 course of 4 hours and an initiator solution of 120 g of
t-butyl perethylhexanoate in 90 g of the aromatic
solvent described was metered into the reactor at a
uniform rate over the course of 4.5 hours. The metered
additions of the monomer mixture and the initiator
10 solution were commenced simultaneously. After the end
of the metered addition of initiator, the reaction
mixture was held at 140°C for a further two hours and
then cooled. The resulting polymer solution had a
solids content of 60%, determined in a forced air oven
15 at 130°C for 1 h, an acid number of 13 mg KOH/g, an OH
number of 116 mg KOH/g, a glass transition temperature
T_g of 3.23°C, and a viscosity of 9 dPas (measured on a
60% dilution of the polymer solution in the aromatic
solvent described, using an ICI cone and plate
20 viscometer at 23°C).

Example 1 and Comparative Experiment C1

The preparation of an inventive one-component clearcoat
25 material (Example 1) and of a noninventive one-
component clearcoat material (Comparative Experiment
C1)

An inventive one-component clearcoat material (Example 1) and a conventional one-component clearcoat material (Comparative Experiment C1) were prepared from the constituents listed in Table 1, by mixing.

5

Table 1: Composition of the inventive one-component clearcoat material (Example 1) and of the conventional one-component clearcoat material (Comparative Experiment C1)

10

Constituents	Example 1 (parts by weight)	Comparative Exp. C2 (parts by weight)
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Binders

Polyacrylate (A) from Preparation Example 2	34.7	50.0
Polyacrylate (A) from Preparation Example 1 (inventive)	15.3	-

Thixotroping paste from Preparation Example 4	3.0	3.0
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Crosslinking agent

TACT	26.6	26.6
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Other constituents:

Substit. Hydroxyphenylbenzo- triazole (95% in xylene) (Tinuvin® 292 from Ciba)	1.0	1.0
Amino ether-modified 2,2,6,6-tetramethylpiper- danyl ester (Tinuvin® 400 from Ciba)	1.2	1.2
Commerical solution of a polyether-modified poly- dimethylsiloxane (5% in xylene) Byk® 310 (Byk Chemie)	1.4	1.4
Butyl diglycol acetate	5.5	5.5
Butyl glycol acetate	5.5	5.5
Solvesso® 150	5.8	5.8
Total:	100	100

TACT = commercial tris(alkoxycarbonylamino)triazine
from CYTEC

- 5 The inventive clearcoat material of Example 1 had a flow time of 23 s in the DIN4 cup at 21°C. In accordance with the invention, it was used as clearcoat material II.
- 10 The noninventive clearcoat material of Comparative Experiment C1 had a flow time of 28 s in the DIN4 cup at 21°C.

Example 2 and Comparative Experiment C2

The production of an inventive multicoat paint system
 5 ML (Example 2) and of a noninventive multicoat paint
 system (Comparative Experiment C2)

For producing the multicoat paint system ML of the
 invention, of Example 2, and the noninventive multicoat
 10 paint system of Comparative Experiment C2, first of all
 a clearcoat material I (undercoat clearcoat) was
 prepared by mixing the constituents indicated in
 Table 2.

15 **Table 2: The composition of the clearcoat material I**

Constituents	Parts by weight
Conventional polyacrylate from Preparation Example 6	43.4
Crosslinking agent from Preparation Example 5	9.0
Commercial butanol- etherified melamine- formaldehyde resin (60% in butanol/xylene)	16.0

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Setalux® C91756 (commercial 13.5
thixotropic agent from
Akzo)

Substituted hydroxyphenyl- 0.6
triazine (65% in xylene)
(Cyagard® 1164L)

Amino ether-modified 0.8
2,2,6,6-tetramethylpiper-
danyl ester (Tinuvin® 123
from Ciba)

Byk® 390 (Byk Chemie) 0.05
Byk® 310 (Byk Chemie) 0.15
Tego® LAG 502 0.2

Butanol 11.4
Solventnaphtha® 2.5
Xylene 0.9
Butyl diglycol acetate 1.5

Total: 100

The clearcoat material I had a flow time of 46 s in the
DIN4 cup at 21°C. For application it was adjusted to a
5 flow time of 28 s using 8 parts by weight of a diluent
(organic solvent mixture).

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In order to produce the test panels, an electrocoat material (dry film thickness 22 μm) and a water-based surfacer (FU63-9400 from BASF Coatings AG) were applied in succession and baked (dry film thickness 30 μm). The
 5 electrocoat material was baked at 170°C for 20 minutes and the surfacer at 160°C for 20 minutes. Then a blue aqueous basecoat material (water percolor basecoat FW 05-513P from BASF Coatings AG) was applied with a film thickness of 15-18 μm and flashed off at 80°C for
 10 10 minutes.

The clearcoat material I (cf. Table 2) was then applied wet-on-wet and baked at 135°C for 30 minutes so as to give a dry film thickness of 35 μm .

15

For Example 2, the test panels obtained in this way were overcoated, without intermediate sanding, with the inventive clearcoat material II (cf. Table 1). The resulting clearcoat film II was baked at 140°C for
 20 20 minutes so as to give a dry film thickness of 20 μm .

For Comparative Experiment C2, the test panels obtained in this way were overcoated, without intermediate sanding, with the noninventive clearcoat material (cf.
 25 Table 1). The resulting clearcoat film II was baked likewise at 140°C for 20 minutes so as to give a dry film thickness of 20 μm .

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The adhesion of the inventive multicoat paint system ML of Example 2 was determined after storage for 24 hours at room temperature, using the crosshatch test in accordance with DIN 53151 (2 mm) [rating 0 to 5]. There
 5 was no delamination: rating GT0. In the case of the noninventive multicoat paint system of Comparative Experiment C2, on the other hand, there was delamination of the clearcoat: rating GT4.

10 The scratch resistance of the multicoat paint system on the test panels was assessed as follows after storage at room temperature for 24 hours, using the BASF brush test which is described in Fig. 2 on page 28 of the article by P. Betz and A. Bartelt, Progress in Organic
 15 Coatings, 22 (1993), pages 27-37, albeit with modification in respect of the weight used (2 000 g instead of the 280 g specified therein):

In the test, the film surface was damaged with a woven
 20 mesh which was loaded with a weight. The woven mesh and the film surface were wetted generously with a laundry detergent solution. By means of a motor drive, the test panel was moved backward and forward under the woven mesh in reciprocating movements.

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The test element was an eraser (4.5 x 2.0 cm, broad side perpendicular to the direction of scratching) around which was stretched a woven nylon mesh (No. 11,

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31 μ m mesh size, Tg 50°C). The applied weight was 2 000 g.

Prior to each test, the woven mesh was replaced, with the running direction of the woven meshes parallel to the direction of scratching. Using a pipette, about 1 ml of a freshly stirred 0.25% Persil solution was applied before the eraser. The speed of rotation of the motor was set so as to perform 80 double strokes within a period of 80 s. After the test, the remaining detergent liquid was rinsed off with cold tap water and the test panels were blown dry with compressed air. Measurements were made of the gloss to DIN 67530 before and after damage and after regeneration (reflow). The direction of measurement was perpendicular to the direction of scratching. The results obtained here are compared with one another in Table 3. They demonstrate the superior scratch resistance and excellent reflow behavior of the inventive multicoat paint system ML.

20

Table 3: The scratch resistance by the brush test, and the reflow behavior

Properties	Example 2	Comparative Experiment
		C2
Initial gloss:	87.5	88.2
Gloss after exposure at room temperature:	79.2	73.3

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Gloss after storage at 40°C		
for two hours:	83.5	76.4
Gloss after storage at 60°C		
for two hours:	83.8	78.3
Reflow 40°C:	51.81	20.81
Reflow 60°C:	55.42	33.56

The adhesion properties of the inventive multicoat paint system ML of Example 2 and of the noninventive multicoat paint system of Comparative Experiment C2 were determined by means of the crosshatch test following exposure to condensation. The results can be found in Table 4. They underscore again the superior bond strength of the inventive multicoat paint system ML.

10

Table 4: Constant condensation climate test (CCC test)^{a)} and adhesion properties of the inventive multicoat paint system ML of Example 2 and of the multicoat paint system of Comparative Experiment 2

15

	Example 2	Comparative Exp. 2
Adhesion by the crosshatch test ^{b)}	GT1	GT5

a) customary method of evaluating the resistance of coating materials to exposure to long-term

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humidity (240 hours, 100% rel. humidity, 40°C,
details in the test specification MKK0001A, issue
A/14.05.1996, available from BASF Coatings AG).
The evaluation is made one hour after the end of
5 condensation exposure.

b) crosshatch to DIN 53151 (2 mm) after 240 hours of
SCC and 24 hours of regeneration; rating 0 to 5:
0 = best score; 5 = worst score

10

Example 3 and Comparative Experiment C3

**The production of an inventive multicoat paint system
ML (Example 3) and of a noninventive multicoat paint
15 system (Comparative Experiment C3)**

For determining the surface properties, a commercial
black aqueous basecoat material (FV95-9108 from BASF
Coatings AG) was applied to vertical steel panels and
20 flashed off at 80°C for 10 minutes. The aqueous
basecoat material was applied in a wet film thickness
such that the dry film thickness after baking was from
12 to 15 μm .

25 The clearcoat material I (cf. Table 2) was then applied
wet-on-wet and baked at 135°C for 30 minutes, giving a
dry film thickness of 35 μm .

For Example 3, the test panels thus obtained, without intermediate sanding, were overcoated in vertical position with the inventive clearcoat material II of Example 1 (cf. Table 1). The resulting inventive clearcoat film II was baked at 140°C for 20 minutes, giving a dry film thickness of 20 μm .

For Comparative Experiment C3, the test panels, without intermediate sanding, were overcoated in vertical position with the noninventive clearcoat material of Comparative Experiment C1 (cf. Table 1). The resulting inventive clearcoat film II was baked likewise at 140°C for 20 minutes, giving a dry film thickness of 20 μm .

The surface properties of the resulting inventive multicoat paint system ML of Example 3 and of the noninventive multicoat paint system of Comparative Experiment C3 were assessed visually and by means of the WaveScan method. The results can be found in Table 5. They demonstrate that the inventive multicoat paint system ML has an outstanding surface which is substantially free from coarse and fine textures.

Table 5: Leveling properties (vertical) of the inventive multicoat paint system ML of Example 3 and of the multicoat paint system of Comparative Experiment C3

Exp. 3		
Leveling (visual)	very smooth	Surface very
	surface	irregular
Leveling (measured by instrument) ^{a)}		
Wavescan/longwave	1.3	12.7
Wavescan/shortwave	1.1	8.8

a) Instrument: Byk/Gardner - Wave scan plus

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Coating material and its use for producing highly scratch-resistant multicoat clearcoat systems

Claims

5

1. A coating material curable thermally and, if desired, with actinic radiation, comprising

10

A) at least one binder containing at least two functional groups (a1) which are able to undergo thermal crosslinking reactions with complementary functional groups (b1) in the crosslinking agent (B), and

15

B) at least one crosslinking agent containing at least two functional groups (b1) which are able to undergo thermal crosslinking reactions with the complementary functional groups (a1) in the binder (A),

20

and also, if desired,

C) at least one constituent which is crosslinkable with actinic radiation,

25

D) at least one photoinitiator,

E) at least one thermal crosslinking initiator,

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F) at least one reactive diluent curable with actinic radiation and/or thermally,

5 G) at least one coatings additive, and/or

H) at least one organic solvent,

10 characterized in that at least one binder (A) contains in copolymerized form at least one olefinically unsaturated polysiloxane macromonomer containing on average per molecule at least 3.0 double bonds.

15 2. The coating material as claimed in claim 1, characterized in that the polysiloxane macromonomer contains on average per molecule at least 4.0, with particular preference at least 5.0, and in particular at least 5.5 double bonds.

20

3. The coating material as claimed in claim 1 or 2, characterized in that the polysiloxane macromonomer contains on average per molecule up to 10.5, preferably 9.0, with particular
25 preference 8.5, and in particular 8.0 double bonds.

4. The coating material as claimed in any of claims 1 to 3, characterized in that the polysiloxane

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macromonomer contains on average per molecule from 5.5 to 6.5, in particular 6.0, double bonds.

5. The coating material as claimed in any of claims 1 to 4, characterized in that the polysiloxane macromonomer has a number-average molecular weight M_n of from 500 to 100 000, preferably from 1 000 to 50 000, with particular preference from 2 000 to 30 000, and in particular from 2 500 to 20 000 daltons.
6. The coating material as claimed in any of claims 1 to 4, characterized in that the polysiloxane macromonomer is in three-dimensionally crosslinked form.
7. The coating material as claimed in any of claims 1 to 5, characterized in that the polysiloxane macromonomer is an alkyl-, cycloalkyl-, alkyl-aryl-, alkyl-cycloalkyl-, cycloalkyl-aryl- or arylsiloxane resin.
8. The coating material as claimed in claim 6, characterized in that the alkyl radicals contain from 1 to 10, with particular preference from 1 to 5, and in particular from 1 to 3 carbon atoms, the cycloalkyl radicals contain from 3 to 10, with particular preference from 4 to 8, and in particular from 5 to 7 carbon atoms, and the aryl

binders (A) contains in copolymerized form at least 0.01% by weight, preferably at least 0.05% by weight, with particular preference at least 0.08% by weight, and in particular at least 0.1% by weight, based in each case on the binder (A), of at least one polysiloxane macromonomer according to any of claims 1 to 9.

13. A multicoat clearcoat system KL for a primed or unprimed substrate, producible by

(1) applying at least one clearcoat film I of a coating material I curable thermally and, if desired, with actinic radiation to the surface of the substrate and

(1.1) partly or

(1.2) fully

curing it, and

(2) applying a further clearcoat film II of a coating material II curable thermally and, if desired, with actinic radiation to the surface of the clearcoat film(s) I

(3) and then curing

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(3.1) the clearcoat films I and II together
or

(3.2) the clearcoat film II alone,

5 thermally and, if desired, with actinic
radiation

characterized in that the coating material II
and/or the coating material I, especially the
10 coating material II, is a coating material as
claimed in any of claims 1 to 11.

14. A process for producing a multicoat clearcoat
system KL on a primed or unprimed substrate by

15

(1) applying at least one clearcoat film I of a
coating material I curable thermally and, if
desired, with actinic radiation to the
surface of the substrate and

20

(1.1) partly or

(1.2) fully

curing it, and

25

(2) applying a further clearcoat film II of a
coating material II curable thermally and, if
desired, with actinic radiation to the
surface of the clearcoat film(s) I

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(3) and then curing

(3.1) the clearcoat films I and II together

5

or

(3.2) the clearcoat film II alone,

thermally and, if desired, with actinic
radiation

10

characterized in that the coating material II
and/or the coating material I, especially the
coating material II, is a coating material as
claimed in any of claims 1 to 11.

15

15. A multicoat color and/or effect paint system ML
for a primed or unprimed substrate, producible by

(1) applying at least one color and/or effect
basecoat film III of a pigmented coating
material III curable thermally and, if
desired, with actinic radiation to the
surface of the substrate, and drying it
without curing,

20

25

(2) applying at least one clearcoat film I of a
coating material I curable thermally and, if
desired, with actinic radiation to the
surface of the basecoat film III, and

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- (2.1) partly curing it alone,
- (2.2) partly curing it together with the
basecoat film III, or
- (2.3) fully curing it together with the
basecoat film III,

thermally and, if desired, with actinic
radiation, and

- (3) applying a further clearcoat film II of a
coating material II curable thermally and, if
desired, with actinic radiation to the
surface of the clearcoat film(s) I,

- (4) and then curing

(4.1) the clearcoat films I and II and the
basecoat film III together or

(4.2) the clearcoat film II alone,

thermally and, if desired, with actinic
radiation,

characterized in that the coating material II
and/or the coating material I, especially the
coating material II, is a coating material as
claimed in any of claims 1 to 11.

(4) and then curing

5 (4.1) the clearcoat films I and II and the
basecoat film III together or

(4.2) the clearcoat film II alone,

thermally and, if desired, with actinic
radiation,

10

characterized in that the coating material II
and/or the coating material I, especially the
coating material II, is a coating material as
claimed in any of claims 1 to 11.

15

17. The use of the coating material as claimed in any
of claims 1 to 11, of the clearcoat system KL as
claimed in claim 12, of the clearcoat system KL
produced as claimed in claim 13, of the multicoat
20 paint system ML as claimed in claim 14, and of the
multicoat paint system produced as claimed in
claim 15 in automotive OEM finishing and
automotive refinish, industrial coating, including
coil coating and container coating, the coating of
25 plastics, and furniture coating.

18. Primed or unprimed substrates comprising at least
one clearcoat system KL as claimed in claim 12,
one clearcoat system KL produced as claimed in

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claim 13, one multicoat paint system ML as claimed
in claim 14 and/or one multicoat paint system ML
produced as claimed in claim 15.

ABSTRACT

The invention relates to a coating material which can be hardened thermally and, optionally, by using actinic radiation. Said coating material contains: A) a binding agent comprising at least two functional groups (a1) which can enter into thermal cross-linking reactions with complementary functional groups (b1) in cross-linking agent (B), and; (B) at least one cross-linking agent comprising at least two functional groups (b1) which can enter into thermal cross-linking reactions with complementary functional groups (a1) in binding agent (A). At least one binding agent (A) contains, in an integrally polymerized manner, at least one olefinically unsaturated polysiloxane macromonomer which contains, in the statistical mean, at least 3.0 double bonds per molecule. The invention also relates to the use of the coating material for producing highly scratch resistant multilayer transparent lacquers.

Please type a plus sign [+] inside this box → +

<p align="center">DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63)</p> <p><input checked="checked" type="checkbox"/> Declaration Submitted with initial Filing or <input type="checkbox"/> Declaration Submitted after initial Filing (surcharge (37 CFR 1.16 (e)) required)</p>		Attorney Docket No.	IN - 5555
		First Named Inventor	Ulrike RÖCKRATH et al.
		COMPLETE IF KNOWN	
		Application Number	
		Filing Date	Thursday, February 14, 2002
		Group Art Unit	
		Examiner Name	

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention **entitled:**

COATING MATERIAL AND ITS USE FOR PRODUCING HIGHLY SCRATCH RESISTANT MULTILAYER
TRANSPARENT LACQUERS

(Title of the Invention)

The specification of which:

☒ is attached hereto

☒ Was filed on **16. August 2000** as United States Application or PCT International Application Number **PCT/EP00/07990**
and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application

I hereby claim foreign priority benefits under 35, U.S.C. § 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate or 365 (a) of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below, by checking the box, any foreign application(s) for patent or inventor's certificate, or any PCT international application(s) having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date DATE/MONTH/YEAR	Priority Not Claimed	Certified Copy Attached?	
				Yes	No
19938759.1	GERMANY	16. August 1999	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Additional foreign application number are listed on a supplemental priority data sheet PTO/SB/02B attached hereto:

I hereby claim the benefit under 35 U.S.C 119(e) of any United States provisional application(s) listed below:

APPLICATION NUMBER(S)	FILING DATE	
		<div data-bbox="995 1438 1062 1444" style="border: 1px solid black; width: 50px; height: 40px; display: inline-block;"></div> <div data-bbox="1076 1438 1425 1449"> Additional provisional application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto </div>

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Name OF SOLE OR FIRST INVENTOR: <u>100</u>				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
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